Synthesis and *X*-Ray Crystal Structures of 2,3-Dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1*H*)-thione 2-Sulphide Derivatives†

R. Morrin Acheson * **and Claire T. Lines**
Department of Biochemistry, South Parks Road, Oxford OX1 3QU
Martin R. Bryce
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE
Zbigniew Dauter and Colin D. Reynolds
Department of Chemistry, University of York, Heslington, York YO1 5DD
Alfred Schmidpeter
Institut für Inorganische Chemie der Universität München, 8000 Munchen 2, West Germany

2-Amino-benzamide or -thiobenzamide, with phosphorus pentasulphide in pyridine, gave the pyridine complex (**1**) of 2,3-dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1*H*)-thione 2-sulphide (**2**), which with alkali and dimethyl sulphate yielded 1,2-dihydro-1-methyl-2,4-bismethylthio-2,1,3-benzophosphadiazine 2-sulphide (**3**). The ^{31}P, ^{13}C, and ^{1}H n.m.r. and mass spectra and some reactions of (**1**) and (**3**) were investigated, and their crystal structures were determined by direct methods.

From attempts to prepare 3-amino-2,1-benzisothiazole (obtainable from 2-aminothiobenzamide with hydrogen peroxide[1]) by treating 2-aminobenzamide with phosphorus pentasulphide in refluxing pyridine, another compound was obtained. Analysis (C, H, N, S) gave data corresponding to the empirical formula $C_{12}H_{11}N_3S_4$, and a subsequent *X*-ray crystal structure analysis suggested that it was a 1:1 molar complex of pyridine with 2,3-dihydro-2,1,3-benzothiadiazine-4(1*H*)-thione 2,2-disulphide.[2]

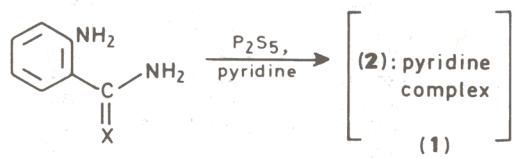
Suspicions were aroused that this structure was not correct when attempted methylation appeared to give a trimethyl derivative, the ^{1}H n.m.r. spectrum of which showed two of the methyl signals as doublets and the third as a singlet. It is now established that the substance is in fact the pyridine complex (**1**) of 2,3-dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1*H*)-thione 2-sulphide (**2**) which differs from the original structure proposed in that one sulphur atom has been replaced by one phosphorous and one hydrogen atom.

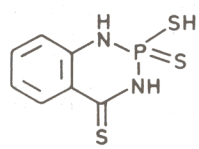
The compound has now been synthesised in high yield by refluxing either 2-amino-benzamide or -thiobenzamide with phosphorus pentasulphide in pyridine. It is not as stable as previously thought[2] and partially decomposes to 2-amino-thiobenzamide on recrystallisation from aqueous dimethylformamide. It gives the expected analytical data for all the elements present and the presence of phosphorus was confirmed by ^{31}P n.m.r. The phosphadiazine itself (**2**) was obtained as a hygroscopic solid from the pyridine complex by coating it on silica, and eluting with appropriate solvents. The use of 2-amino-*N*-methylbenzamide similarly gave the analogue (**6**).

Refluxing 2-aminobenzamide in toluene (instead of pyridine) with phosphorus pentasulphide gave 2-(2-aminophenyl)-4(1*H*)-quinazolone (**9**) and no trace of the phosphadiazine (**2**); adding 2 moles of pyridine before refluxing gave only the quinazolone and none of the phosphadiazine (**1**). The synthesis failed when the pyridine was replaced by 3-bromo- or 3-chloro-pyridine, or triethylamine, but was successful when 2,6-dimethylpyridine was employed; heating the resulting complex with pyridine gave (**1**).

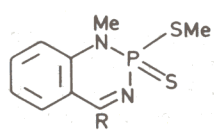
Oxidation of the complex (**1**) by acidified potassium permanganate, or of the phosphadiazine (**2**) by alkaline permanganate, gave 2-aminothiobenzamide, and attempted desulphurisation by Raney nickel yielded a mixture of the same thioamide and 2-aminobenzamide. The complex (**1**) with dimethyl acetylenedicarboxylate in dimethylformamide gave tetramethyl 4*H*-quinolizine-1,2,3,4-tetracarboxylate[3] and the phosphadiazine (**2**), identified by chromatographic comparison with authentic materials.

Treatment of the complex (**1**) with cold aqueous alkali, removal of the pyridine in ether, and methylation of the aqueous





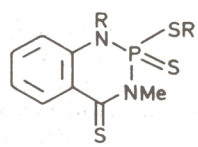
(**2**)



(**3**) R = SMe

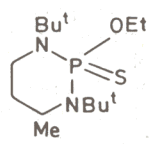
(**4**) R = —N

(**5**) R = -NH

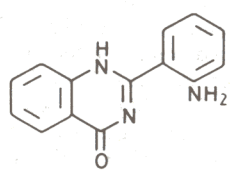


(**6**) R = H, pyridine complex

(**7**) R = Me



(**8**)



(**9**)

† *Supplementary data available* (No. SUP 56335, 10 pp.): thermal parameters, bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1. Structure factors are available from the editorial office.

Table 1. N.m.r. spectra (δ) of the complex (**1**), pyridine (A),[a] pyridinium iodide (B), and 1-methylpyridinium iodide (C)[a] in $(CD_3)_2SO$

	Pyridine resonances					
Compound	2-H	3-H	4-H	2-C	3-C	4-C
(**1**)	8.54	7.74	8.27	143.7	126.3	133.0
(A)	8.22	6.85	7.23	149.7	123.8	135.4
(B)	8.92	8.06	8.60	146.3	127.3	142.4
(C)	9.10	8.20	8.68	145.5	127.7	145.1

[a] For ^{13}C spectra in other solvents see F. A. L. Anet and I. Yavari, *J. Org. Chem.*, 1976, **41**, 3589.

Table 2. Atomic co-ordinates (× 10^4) for (**1**) (e.s.d.s in parentheses)

Atom	*x*	*y*	*z*
C(1)	7 263(5)	833(8)	−2 028(6)
C(2)	8 547(4)	1 582(8)	−1 349(6)
C(3)	9 366(5)	1 624(9)	−1 955(6)
C(4)	8 914(5)	1 031(9)	−3 278(7)
C(5)	7 651(6)	438(10)	−4 028(7)
C(6)	6 844(5)	316(8)	−3 407(7)
C(7)	6 407(5)	432(8)	−1 252(6)
S(8)	4 922(1)	−842(3)	−1 849(2)
N(9)	6 843(4)	1 046(7)	29(5)
P(10)	8 174(1)	2 843(2)	534(2)
N(11)	9 012(4)	2 194(7)	−23(5)
S(12)	7 792(1)	5 576(2)	−789(2)
S(13)	8 858(1)	2 226(3)	2 827(2)
N(14)	7 597(9)	5 433(12)	2 877(11)
C(15)	8 239(8)	5 658(14)	4 325(12)
C(16)	7 684(9)	6 062(13)	5 071(10)
C(17)	6 437(9)	6 174(16)	4 315(12)
C(18)	5 787(8)	5 922(16)	2 825(12)
C(19)	6 403(9)	5 622(13)	2 098(11)

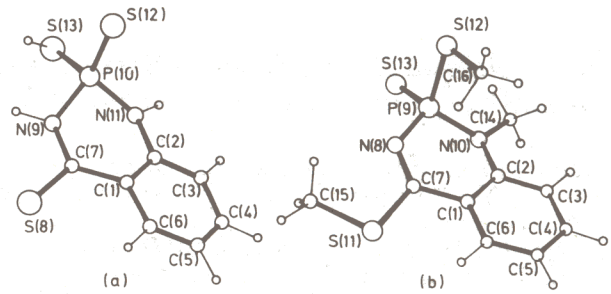


Figure 1. Equivalent views of the molecular structures of (a) (**1**) and (b) (**3**) with the atom-numbering schemes. The pyridine molecule of (**1**) is not shown; its atom-numbering scheme is given in ref. 2.

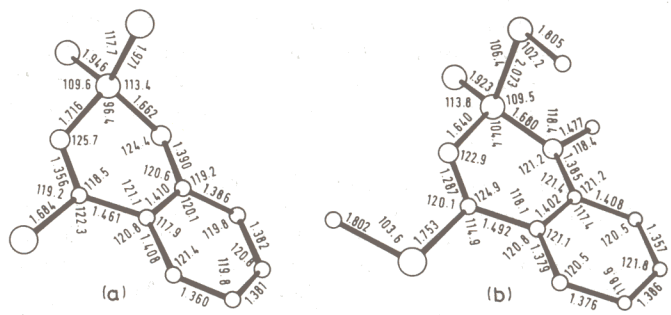


Figure 2. Bond lengths and angles for (a) (**1**) and (b) (**3**). Angles not shown (a) N(9)–P(10)–S(12) 107.8° and N(11)–P(10)–S(13) 109.9°; (b) N(8)–P(9)–S(12) 109.6° and N(10)–P(9)–S(13) 113.1°. The bond lengths within the pyridine molecule of (**1**) were kept fixed: C–C 1.392 and C–N 1.349 Å. The e.s.d.s for the bond lengths and angles for (**1**) are in the range 0.002—0.012 Å, 0.2—0.8° and for (**3**) 0.004—0.015 Å, 0.3—1.0°

solution with dimethyl sulphate or methyl iodide gave the trimethyl derivative (**3**). Methylation of (**6**) gave the corresponding trimethyl derivative (**7**). Heating the trimethylated compound (**3**) with pyrrolidine or aniline expelled methanethiol, with formation of the amines (**4**) and (**5**), respectively, by breaking a carbon–sulphur bond.

The ^1H n.m.r. spectrum of the complex (**1**) showed two N–*H* peaks as doublets, due to coupling with phosphorus. Two-dimensional correlated spectroscopy (COSY) studies showed the coupling pattern between the aromatic protons, and that the N–*H* protons did not couple with each other. The S–*H* proton was not detected. The spectrum of the pyridine complex was also examined in detail at 300 MHz; the proton couplings were confirmed, but again the SH signal could not be found. There is, however, evidence from the *X*-ray analysis of (**1**) for the S–*H* proton. The highest peak in the difference Fourier map calculated after least-squares refinement of all the other atoms was at a sensible bonding distance from S(13). Refinement of the position of this (possible) hydrogen atom gave a final S(13)–H(13) bond distance of 1.11(11) Å, although the P(10)–S(13)–H(13) angle was only 69.2(6.1)°.

A comparison of the resonance positions for the protons of the pyridine ring in pyridine, pyridinium iodide, 1-methylpyridinium iodide, and the complex (**1**) (Table 1) suggests that some transfer of positive charge to the pyridine nitrogen in the complex does occur, but nothing like that required by a complete proton transfer. A similar comparison of the ^{13}C resonances (Table 1) gives a less clear picture, but the 4-C resonances for (**1**) and pyridine are at significantly higher field than that of pyridinium iodide, or of 1-methylpyridinium iodide where the charge, and not the methyl group, would be expected to be the major cause of the downfield shift of the 4-C resonance. The positions of the N–*H* signals are concentration dependent but the C–*H* resonance positions differ little between (**1**) and (**2**), confirming that there is little apparent interaction between the pyridine and phosphadiazine ring systems in (**1**). The ^{13}C resonances of the corresponding atoms of (**1**) and (**2**) are very similar.

The ^{31}P resonances for (**1**) and the trimethylphosphadiazine (**3**) are at +63.3 and +64.9 p.p.m., respectively, perhaps remarkably close to that of trimethylphosphine sulphide (+59).[4]

The ^1H n.m.r. spectrum of the trimethyl derivative (**3**) showed three high-field methyl resonances, two coupled (*J* 10 and 16 Hz) and one not coupled to phosphorus; the last (at δ 2.50) was absent in the spectra of the amines (**4**) and (**5**) and was therefore due to the *S*-methyl group at position 4. The lower-field doublet is due to the *N*-methyl group; the coupling with phosphorus is almost the same as that in (**6**). In the trimethyl derivative (**7**) all the methyl groups couple with phosphorus. The lowest-field signal would be expected to be due to that at position 3; its coupling with phosphorus is the same as that shown by the methyl group in (**6**).

Views of the molecular structures of (**1**) and (**3**) are shown in Figure 1(a) and (b), respectively. Final atomic positional and thermal parameters are given in Tables 2 and 3, and bond distances and angles are shown in Figures 2(a) and (b) for (**1**) and (**3**) respectively.

The phosphadiazine ring adopts a distorted half-chair conformation in both (**1**) and (**3**), with the phosphorus atom 0.59 and 0.36 Å, respectively, out of the mean plane through the

Table 3. Atomic co-ordinates (× 10^4) for (**3**) (e.s.d.s in parentheses)

Atom	*x*	*y*	*z*
C(1)	5 392(6)	5 432(8)	7 711(15)
C(2)	5 986(6)	6 315(8)	8 305(15)
C(3)	5 689(6)	7 516(8)	8 290(16)
C(4)	4 870(8)	7 796(11)	7 699(19)
C(5)	4 290(7)	6 921(9)	7 077(18)
C(6)	4 555(7)	5 734(10)	7 141(15)
C(7)	5 685(7)	4 145(8)	7 762(14)
N(8)	6 497(5)	3 790(6)	7 946(11)
P(9)	7 320(2)	4 723(2)	8 341(1)
N(10)	6 820(5)	6 013(7)	8 915(14)
S(11)	4 827(2)	3 094(2)	7 572(6)
S(12)	8 047(2)	5 001(2)	6 124(6)
S(13)	8 143(2)	4 138(8)	10 223(6)
C(14)	7 365(7)	6 965(9)	9 707(21)
C(15)	5 400(8)	1 674(10)	7 704(21)
C(16)	7 210(8)	5 550(11)	4 655(19)

other atoms in the heterocyclic ring. The geometry at the phosphorus atom is approximately tetrahedral in (**3**) with a P–S single-bond distance of 2.073(4) Å and a P=S double-bond distance of 1.923(4) Å. The bond angles around the P atom range from 104.4(4) to 113.8(3)°, with a S–P–S angle of 106.4(2)°. The complex (**1**) shows a greater distortion from tetrahedral geometry at the P atom, with P–S bond distances of 1.946(2) and 1.971(2) Å, and bond angles varying from 96.4(3) to 117.7(1)°, the S–P–S angle having increased to 117.7(1)°. The endocyclic P–N distances in (**1**) and (**3**) vary from 1.640(8) to 1.716(4) Å and are all shorter than the expected P–N single-bond distance of 1.77 Å.[5] The N–P–N bond angles are 96.4(3) and 104.4(4)° in (**1**) and (**3**) respectively. The S–P–N angles are in the range 107.8(2) to 113.8(3)°, in good agreement with reported values.[5] The only other compound closely analogous to (**1**) and for which structural data are available is (**8**).[6] The P–S and P–N distances [1.949(3), 1.668(5), and 1.645(6), respectively] are very similar to those of (**1**) (Figure 2). The sulphur-containing part of (**1**) is linked to the pyridine molecule *via* a hydrogen bond between S(13) and N(14), with a S(13) ... N(14) distance of 3.32 Å. Hydrogen bonds of this type do not seem to be common.[7]

Experimental

N.m.r. spectra are for $(CD_3)SO$ solutions [δ_H (*J*/Hz) from Me_4Si at 60 MHz; δ_P from H_3PO_4 at 101.23 MHz] unless otherwise stated. Phosphorus pentasulphide was purified by Soxhlet extraction with carbon disulphide.

Preparation of the Pyridine Complex (**1**) *of* 2,3-*Dihydro*-2-*mercapto*-2,1,3-*benzophosphadiazine*-4(1H)-*thione* 2-*Sulphide*.—(i) Phosphorus pentasulphide (3 g) was added to 2-aminothiobenzamide (2 g) in pyridine (15 ml). The mixture was refluxed for 1.5 h, then allowed to cool and poured into ice–water (50 ml). The yellow precipitate was filtered off and dried giving the *pyridine complex* (**1**) (3.6 g, 85%), yellow crystals (rapidly from dimethylformamide–water), m.p. 213—215 °C (Found: C, 44.3; H, 3.9; N, 12.8; P, 9.3; S, 29.6. $C_{12}H_{12}N_3PS_3$ requires C, 44.3; H, 3.7; N, 12.9; P, 9.5; S, 29.5%); $\nu_{max.}$(Nujol) 1 607, 1 570, 1 190—1 179br, 1 158, 1 132, 992, 899, 747, 681, and 663 cm^{-1}; δ_H (300 MHz) (pyridine moiety) 8.94 (2 H, q, *J* 6.5 and 1.4, 2-H), 8.60 (1 H, m, 4-H), and 8.07 (2 H, q, *J ca.* 6.4 and 6.7, 3-H); (benzophosphadiazine moiety) 11.5 [1 H, br, 3- (or 1-) H], 10.44 [1 H, br d, $J_{P,C}$ 10.8, 1- (or 3-) H] (1-H and 3-H are deuterium-exchangeable, positions vary a little with concentration, and these protons have been observed at 60 MHz to give a single broad peak centred on δ 10.7), 8.27 (1 H, q, *J* 8.1 and 1.4, 5-H), 7.27 (1 H, t, *J ca.* 7.5, 7-H), 6.84 (1 H, d, *J* 7.8, 8-H), and 6.74 (1 H, t, *J ca.* 7.4, 6-H). Irradiation at δ 6.74 caused the quartet at δ 8.27 to collapse to a singlet, and irradiation at δ 8.27 caused the expected change to the triplet at δ 6.74. For the phosphadiazine system, δ_C 191.0 (s, 4-C), 141.5 (s, 4a-C), 133.9 (d, 8-C), 133.0 (d), 121.2 (s, 8a-C), 118.1 (d), and 117.6 (d) (all resonances show some coupling with P); for the pyridine system 143.7 (d, 2-C), 133.0 (d, 4-C), and 126.3 (d, 3-C); δ_P 63.3 (s, 2-P).

(ii) Phosphorus pentasulphide (5.9 g) was refluxed with 2-aminobenzamide (3.6 g) in pyridine (15 ml) for 1.5 h. The product was worked up as in (i) to give (**1**) (7.72 g, 90%) with the properties already described.

(iii) Phosphorus pentasulphide (2.0 g), 2-aminobenzamide (1.0 g), and 2,6-dimethylpyridine (15 ml) were refluxed for 1.5 h, cooled, and poured into ice–water (100 ml). Basification with M-sodium hydroxide (200 ml) and just acidifying with aqueous M-hydrochloric acid precipitated 2,3-dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1*H*)-thione 2-sulphide 2,6-dimethylpyridine complex (0.5 g), m.p. 222—223 °C, which could not be recrystallised; δ_H (90 MHz) (benzophosphadiazine part) 10.35 (1 H, br d, NH), 8.40 (1 H, br s, NH), 7.97 (1 H, d, *J ca.* 7, 5-H), 7.01 (1 H, t, *J ca.* 7 + 7, 7-H), 6.42—6.65 (2 H, m, 6- and 8-H); pyridine part: 7.90 (1 H, t, *J ca.* 7, 4-H), 7.34 (2 H, d, *J* 7, 3- and 5-H), and 2.34 (6 H, s, 2,6-Me_2).

Heating this compound in pyridine and pouring into water precipitated mainly (**1**), identified from its ^1H n.m.r. spectrum, and methylation (0.5 g) as for (**1**) using aqueous sodium hydroxide and dimethyl sulphate gave (**3**) (0.2 g), identical with the analysed specimen.

2,3-*Dihydro*-2-*mercapto*-2,1,3-*benzophosphadiazine*-4(1H)-*thione* 2-*Sulphide* (**2**).—(i) The pyridine complex (**1**) (500 mg) was refluxed in acetone (100 ml) for 5 min; silica (10 g) was added, the acetone removed *in vacuo*, and the residue placed on top of a six-inch silica column previously washed with methanol (10%) in ethyl acetate. Elution with this solvent gave first 2-aminothiobenzamide, identified from its ^1H n.m.r. spectrum, followed by the phosphadiazine (**2**) (200 mg, 40%; elution was completed by a 1 : 1 solvent mixture), a hygroscopic yellow solid, m.p. 170—172 °C, δ_H (470 MHz) (COSY) 10.55 (1 H, d, $J_{P,H}$ 13.2, NH), 8.76 (1 H, d, $J_{P,H}$ 11.8, NH), 8.56 (1 H, d, 5-H), 7.53 (1 H, t, 7-H), 7.10 (1 H, t, 8-H), and 6.98 (1 H, d, 6-H); δ_C 191.2 (s, 4-C), 142.0 (s, 4a-C), 133.5 (2 C, d), 121.7 (s, 8a-C), 118.3 (d), and 117.8 (d) (all resonances show small coupling with P).

(ii) The pyridine complex (3.0 g) was dissolved in aqueous M-sodium hydroxide (100 ml) and the solution was extracted three times with ether. The dissolved ether was removed from the aqueous layer *in vacuo* and acidification effected with aqueous M-hydrochloric acid. The sulphide (**2**) (0.3 g) precipitated.

Oxidation of the Complex (**1**).—The complex (**1**) (2 g) was refluxed for 1 h with acidified potassium permanganate (1 g). The solution was allowed to cool and then decolourised (to yellow) with aqueous sodium hydrogen sulphite. It was then extracted 3 times with dichloromethane and the dichloromethane was removed *in vacuo* yielding 2-aminothiobenzamide (400 mg, 55%), identified by t.l.c. and ^1H n.m.r. comparisons with authentic material.

(ii) The pyridine complex (**1**) (4 g) was dissolved in aqueous M-sodium hydroxide (100 ml) and extracted three times with ether, the extract being discarded. The ether in the aqueous layer was removed *in vacuo* and potassium permanganate (2 g) added, resulting in an exothermic reaction. The mixture was stirred for 1 h, decolourised with aqueous sodium hydrogen sulphite, and extracted with dichloromethane. Evaporation of the extract yielded 2-aminothiobenzamide, identified as before.

Disulphurisation of the Complex (**1**).—The complex (**1**) (1 g) was refluxed for 1 h with W-10 Raney nickel (three spatulas full) in ethanol (30 ml); the mixture was filtered hot, then left to cool, and water (30 ml) was added. Extraction with ether yielded a mixture of 2-aminothiobenzamide and 2-aminobenzamide, identified from its ^{1}H n.m.r. spectrum and t.l.c. comparisons with authentic materials.

Reaction of the Complex (**1**) *with Dimethyl Acetylenedicarboxylate.*—The complex (**1**) (2.0 g) was stirred with the ester (3.0 g) in *N,N*-dimethylformamide (10 ml) or acetonitrile for *ca.* 15 h. T.l.c. of the resulting solutions showed only the presence of the sulphide (**2**) and tetramethyl 4*H*-quinolizine-1,2,3,4-tetracarboxylate (by comparison and co-chromatography with authentic materials).

Reaction of 2-Aminobenzamide with Phosphorus Pentasulphide in Toluene.—Phosphorus pentasulphide (3 g) was refluxed with 2-aminobenzamide (2 g) in toluene (15 ml) for 1.5 h. The solution was allowed to cool, poured into ice–water, and basified. It was then made weakly acidic to yield a yellow precipitate of 2-(2-aminophenyl)-4(1*H*)-quinazolone (**9**) (0.6 g, 16.9%), m.p. 247—250 °C (from dimethylformamide–water) (Found: C, 70.7; H, 4.7; N, 17.6. Calc. for $C_{14}H_{11}N_3O$: C, 70.9; H, 4.6; N, 17.7%), *m/z* (in beam electron ionisation) 237 (100, M^+), 119 (75, M^+ − 2-aminobenzonitrile), and 92 (24). Mixed m.p. and spectral comparisons showed the compound to be identical with authentic material, prepared as described [8] and of m.p. 245—246 °C (lit., 241 °C). The procedure was repeated with the addition of pyridine (2.3 g), and only gave 0.2 g (5.6%) of the same quinazolone.

1,2-*Dihydro*-1-*methyl*-2,4-*bismethylthio*-2,1,3-*benzophosphadiazine* 2-*Sulphide* (**3**).—The pyridine complex (**1**) (12 g) was dissolved in aqueous M-sodium hydroxide (200 ml) and the resulting solution was extracted three times with ether. The aqueous solution, cooled to 0 °C, was stirred for 0.5 h with dimethyl sulphate (20 ml), giving a yellow precipitate which was filtered off, dried and recrystallised (from *ca.* 20 ml of nitromethane) to yield the *trimethyl derivative* (**3**) (4.8 g, 45%), m.p. 140—142 °C (Found: C, 41.9; H, 4.7; N, 9.9; S, 33.0; P, 11.1. $C_{10}H_{13}N_2PS_3$ requires C, 41.7; H, 4.2; N, 9.7; S, 33.3; P, 11.0%); *m/z* 288 (46, M^+), 241 (100, M^+ − SMe), 209 (45, M^+ − SMe − S) [for M^+ 100%, M + 1 is 14.52 and M + 2 14.11%; $C_{10}H_{13}N_2S_3P$ requires M + 1 14.50, M + 2 14.29%]; δ_H (300 MHz) 7.90 (1 H, q, *J* 8.0 + 1.4, 5-H), 7.55 (1 H, t, *J* 2 × *ca.* 8 + 2 × 1.4, 7-H), 7.07 (1 H, d, *J* 8.7, 8-H), 6.99 (1 H, t, 6-H), 3.37 (3 H, d, $J_{P,H}$ 10, 4-Me), 2.60 (3 H, s, 4-Me), and 2.08 (3 H, d, $J_{P,H}$ 16); δ_C 177.6 (s, $J_{P,C}$ 14.7, 4-C), 143.4 (s, 4a-C), 135.9 (d, Ar-C), 127.2 (d, Ar-C), 120.8 (d, Ar-C), 116.9 (s, $J_{P,C}$ 22, 8a-C), 115.3 (d, $J_{P,C}$ 5, 8-C?), 31.8 (q, $J_{P,C}$ 3, 1-*C*H$_3$), 15.3 (q, $J_{P,C}$ 5, 2-S*C* H$_3$), and 13.2 (q, $J_{P,C}$ 0, 4-S*C*H$_3$).

1,2-*Dihydro*-1-*methyl*-2-*methylthio*-4-*pyrrolidino*-2,1,3-*benzophosphadiazine* 2-*Sulphide* (**4**).—The trimethyl derivative (**3**) (0.5 g) was refluxed for 1 h with pyrrolidine (2 ml). On cooling, the *amine* (**4**) (0.4 g, 76%) precipitated; recrystallisation (from nitromethane) gave colourless plates, m.p. 157—158 °C (Found: C, 50.6; H, 5.6; N, 13.2. $C_{13}H_{18}N_3PS_3$ requires C, 50.2; H, 5.8; N, 13.5%); δ_H 6.71—7.33 (4 H, m, 5-, 6-, 7-, and 8-H), 3.3—3.7 (4 H, m, N[CH_2]$_2$), 3.02 (3 H, d, $J_{P,C}$ 11, 1-Me), 1.78 (3 H, d, $J_{P,C}$ 16, 2-SMe), and 1.4—1.9 (4 H, br m, [CH_2]$_2$); *m/z* (chemical ionisation NH_3) 312 (100, M^+ + 1).

4-*Anilino*-1,2-*dihydro*-1-*methyl*-2-*methylthio*-2,1,3-*benzophosphadiazine* 2-*Sulphide* (**5**).—The trimethyl derivative (**3**) (0.5 g) was refluxed for 1 h with aniline (15 ml). The solution was allowed to cool and the aniline distilled off under vacuum. The residue was shaken with ethanol (30 ml) and left for 48 h. The precipitate of the *amine* (**5**) was filtered off (0.2 g, 35%), dried, and recrystallised (from nitromethane) to give pale yellow needles, m.p. 177—178 °C (Found C, 54.5; H, 4.9; N, 12.3. $C_{15}H_{16}N_3PS_2$ requires C, 54.1; H, 4.8; N, 12.6%); δ_H 8.11 (1 H, d, *J* 8, 5-H), 6.95—7.85 (9 H, m, Ar-H and N-H; N-H exchanges with D_2O), 3.22 (3 H, d, $J_{P,H}$ 10.5, 1-Me), and 1.95 (3 H, d, $J_{P,H}$ 14.5, 2-SMe); *m/z* (chemical ionisation, NH_3) 334 (100%, M + 1) and 250 (25).

The Pyridine Complex (**6**) *of* 2,3-*Dihydro*-2-*mercapto*-3-*methyl*-2,1,3-*benzophosphadiazine*-4(1H)-*thione* 2-*Sulphide.*—This was prepared as for (**1**), but replacing 2-aminobenzamide by 2-amino-*N*-methylbenzamide (obtained as and with the properties described [9]) as a yellow substance (1.2 g), m.p. 168—169 °C, which decomposed on attempted purification; δ_H (90 MHz) (phosphadiazine part) 9.08 (1 H, br s, 1-H, exchanges with D_2O), 8.09 (1 H, d, *J* 7.5, 5-H), 7.15 (1 H, t, *J* 7.5 + 7.5, 7-H), 6.78 (1 H, d, *J* 7.5, 8-H), 6.64 (1 H, t, *J* 7.5 + 7.5, 6-H), and 3.53 (3 H, d, $J_{C,P}$ 9, 3-Me); (pyridine part) 8.61 (2 H, d, *J ca.* 6, 2-H_2), 8.19 (1 H, t, *J* ca. 7, 4-H), and 7.66 (2 H, t, *J ca.* 6, 3-H_2); *m/z* 260 (3, M^+), 227 (2, M^+ − SH), and 79 (100, pyridine).

2,3-*Dihydro*-1,3-*dimethyl*-2-*methylthio*-2,1,3-*benzophosphadiazine*-4(1H)-*thione* 2-*Sulphide* (**7**).—The complex (**6**) (1.0 g) was methylated as for (**1**) using sodium hydroxide and dimethyl sulphate to give the trimethyl compound (**7**) as a very hydroscopic yellow solid (0.6 g), m.p. *ca.* 50 °C, δ_H (90 MHz) 8.47 (1 H, d, *J* 7.5, 5-H), 7.58 (1 H, t, *J* 7.5 + 7.5, 7-H), 6.95—7.30 (2 H, m, 6- and 8-H), 3.72 [3 H, d, $J_{P,H}$ 9, 3- (or 1-) CH_3], 3.42 [3 H, d, $J_{P,H}$ 12, 1- (or 3-) CH_3], and 2.12 (3 H, d, $J_{P,C}$ 17.5, 2-CH_3); *m/z* 290 (4, M^+ + 2), 289 (4, M^+ + 1), 288 (25, M^+), 273 (11, M^+ − Me), 241 (48, M^+ − SCH_3), 209 (15, M^+ − SMe − S), and 168 (100%).

X-*Ray Crystal-structure Determinations.*—Crystal data of (**1**): $C_7H_7N_2PS_3{\cdot}C_5H_5N$, M_r = 325.43, triclinic, space group $P\bar{1}$, a = 12.391(3), b = 7.422(2), c = 10.001(2) Å, α = 64.11(2), β = 117.21(2), γ = 111.79(2)°, U = 719.5 Å^3, Z = 2, F(000) = 335, D_c = 1.50 g cm^{-3}, μ(Cu-K_α) = 54.7 cm^{-1}. Bright yellow crystal (from ethanol) of dimensions 0.30 × 0.20 × 0.15 mm. Crystal data of (**3**): $C_{10}H_{14}N_2PS_3$, M_r = 289.4, orthorhombic, space group $Pna2_1$, a = 15.037(4), b = 11.118(2), c = 7.818(2) Å, U = 1 307.8 Å^3, Z = 4, D_c = 1.47 g cm^3, F(000) = 604, μ(Cu-K_α) = 59.2 cm^{-1}. Pale yellow crystal (from nitromethane) of size 0.25 × 0.20 × 0.50 mm.

Intensity data for both (**1**) and (**3**) were collected with a Hilger and Watts Y290 four-circle diffractometer controlled by a microcomputer. Space group and initial cell parameters were determined from Weissenberg photographs. Accurate unit-cell dimensions were obtained by a least-squares refinement of the θ-values of twenty reflections measured with the four-circle diffractometer. The w−2θ scanning mode was used. For (**1**) 1 713 reflections with $\theta \leqslant 60$ °C and $I \geqslant 2\sigma(I)$ and for (**3**) 665 reflections with $\theta \leqslant 51°$ and $I \geqslant 2\sigma(I)$ were considered as observed. For both data sets corrections for Lorentz and polarization effects and absorption were made.[10]

Structure Solution and Refinement.—Structures (**1**) and (**3**) were determined by direct methods using the program MULTAN 80.[11] The structures were refined by full-matrix least-squares methods (SHELX 76).[12] Atomic scattering factors and anomalous dispersion corrections were taken from International Tables.[13] Anisotropic thermal parameters were included in the final cycles for all non-hydrogen atoms. The bond lengths within the pyridine molecule of (**1**) were kept fixed during the refinement because of high thermal vibrations. All hydrogen atoms were included at calculated positions and methyls were

treated as rigid groups. The refinement for (**1**) converged at $R = 0.066$, $R_w = 0.076$ for 1 710 observed reflections, and for (**3**) at $R = 0.048$, $R_w = 0.051$ for 663 observed reflections.

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References

1 R. F. Meyer, B. L. Cummings, P. Bass, and H. O. J. Collier, *J. Med. Chem.*, 1965, **8**, 515.
2 R. M. Acheson, M. R. Bryce, S. Das, Z. Dauter, A. J. Rees, and C. D. Reynolds, *J. Chem. Soc., Chem. Commun.*, 1983, 1002.
3 R. M. Acheson and G. A. Taylor, *J. Chem. Soc.*, 1960, 1691.
4 L. D. Quin, 'The Heterocyclic Chemistry of Phosphorus,' Wiley, New York, 1981, p. 201.
5 L. E. Sutton (ed.), 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' The Chemical Society, London, 1968.
6 N. V. Belov, V. V. Ilyuhin, V. R. Kalinin, A. I. Zavalishina, A. A. Borisenko, E. I. Smirnova, and Z. E. Nifantlyev, *Dokl. Akad. Nauk. S.S.S.R.*, 1981, **258**, 344.
7 A. F. Wells, 'Structural Inorganic Chemistry,' 4th edn., Clarendon Press, Oxford, 1975, p. 304.
8 R. Pater, *J. Heterocycl. Chem.*, 1971, **8**, 699.
9 M. Körner and A. Weddige, *J. Prakt. Chem.*, 1887, **36**, 141.
10 A. C. T. North, D. C. Phillips, and F. A. Mathews, *Acta Crystallogr., Ser. A*, 1968, **24**, 35.
11 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, 'MULTAN 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data Universities of York and Louvain,' 1980.
12 G. M. Sheldrick, 'SHELX 76, Program System for Crystal Structure Determination,' University of Cambridge, 1976.
13 'International Tables for X-ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

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